PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BPX 9647	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB 03/02100	International filing date *(day/month/year)* 15.05.2003	Priority date *(day/month/year)* 13.06.2002
International Patent Classification (IPC) or both national classification and IPC E21B37/06		
Applicant BP EXPLORATION OPERATING COMPANY LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 9 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☒ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
17.12.2003	14.04.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Mayne, J Telephone No. +49 89 2399-8572

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB 03/02100

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-19 as originally filed

Claims, Numbers

1-29 filed with telefax on 04.02.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 30
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

   ☐ the entire international application,

   ☐ claims Nos.

   because:

   ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):

   ☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

   ☒ the claims, or said claims Nos. 9-14 are so inadequately supported by the description that no meaningful opinion could be formed.

   ☐ no international search report has been established for the said claims Nos.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/ or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

   ☐ the written form has not been furnished or does not comply with the Standard.

   ☐ the computer readable form has not been furnished or does not comply with the Standard.

IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees, the applicant has:

   ☐ restricted the claims.

   ☐ paid additional fees.

   ☐ paid additional fees under protest.

   ☐ neither restricted nor paid additional fees.

2. ☒ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

   ☐ complied with.

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☒ all parts.

☐ the parts relating to claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8, 15-29
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-8, 15-29
Industrial applicability (IA)	Yes:	Claims	1-8, 15-29
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item III
Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

Article 5 PCT

According to the Applicant's letter of 4.3.04 the process of claim 9 is "not a comminution technique. Instead, high shear mixing prevents the particles of the microgel from growing to a mean particle size of 1 μm or greater".

In examples 2-4 (p. 14) after reaction of the polyacrylic acid and polyvinyl alcohol in the presence of a strong acid the wet solid is dried and comminuted (p. 14, l. 20-25).
After size reduction the particles are suspended in water. The D50 of the suspended particles in example 4 is 19.60 μm. Since this is the average particle size **after** size reduction the particle size achieved by the conditions during the reaction must have been higher than 19.60 μm and hence much higher than 1 μm.
In example 5 (p. 15) after reaction of the Bellasol S50™ and polyvinyl alcohol in the presence of a strong acid the solid is wet milled (p. 16, l. 9-12). As can be seen from Table 2 it needs considerable milling to achieve a D50 of less than 1 μm. Even after 170 min comminution, steps 1-10, the D50 is 5.355 μm.

It is nowhere explained in the application how to perform the reaction between the esterifiable scale inhibitor and the polyol under high shear conditions so that a microgel having a mean particle diameter of less than 1 μm is formed.
It is therefore not known how to perform the method of claim 9. An objection of insufficiency of disclosure is raised against claim 9.

No opinion on novelty, inventive step or industrial applicability can be given for claim 9 and its dependent claims 10-14 for this reason.

Re Item IV
Lack of unity of invention

The present application does not fulfill the requirements of Rule 13.1 PCT. The reasons are as follows:

Claim 1 is concerned with particles of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links, the particle having a mean diameter of less than 1 μm.

Claim 23 concerns a method of scale inhibition in a subterranean formation.
An aqueous suspension of scale inhibitor particles with a mean diameter less than 1 μm is injected into a formation through an injection well.
The suspension percolates through the formation towards a production well. The scale inhibitor particles are controllably released in the near bore well region of the production well.

Claim 23 does not mention that the scale inhibitor is an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links.

The common concept linking independent claims 1 and 23 is:

- particles of a scale inhibitor with a mean diameter of less than 1 μm.

This concept is known from D1 (col. 2, l. 35-44 and col. 3, l. 6-13) see §V for detailed discussion.
There is therefore no novel concept which links claims 1 and 23. The requirements of unity of invention are therefore not met.

Re Item V
Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US-B1-6 380 136
D2: US-A-5 089 150

Article 33(2) and (3) PCT

Claim 1 and 20

D2 discloses a scale inhibitor which is cross-linked with a polyalcohol to extend its lifetime (col. 2, l. 17-19). The scale inhibitor can be a carboxylated polymer and cross-linking occurrs by esterification of the carboxylic acid (col. 2, l. 19-20, 38-41).
D2 does not explicitly mention that the scale inhibitor is in the form of particles nor does it mention a suspension of particles. In example 5 of D2 a solution of the scale inhibitor in sea water is used to assess effectiveness.

Claims 1 and 20 are therefore novel.

It is, however, known from D1 that a scale inhibitor can be provided in the form of solid particles and that these particles can be provided as a suspension in a liquid phase (col. 2, l. 35-44).
The particle size in the suspension may be 100% less than 10 μm, preferably 100% less than 7 μm and especially 100% less than 5 μm. Preferably the particle size in the suspension is not less than 25 nm and advantageously not less than 200 nm.
Although the average particle size in the suspension in D1 is usually between 1 and 3 μm D1 provides for particle sizes considerably less than 1 μm.
D1 discloses a suspension of inhibitor particles with an average size of 0.4-1.0 μm (col. 3, l. 6-13).
It would be obvious to a skilled person that the scale inhibitor of D2 could also be made available in these forms. Nothing critical or unexpected has been demonstrated for these features.

Claims 1 and 20 do not fulfill the requirements of Article 33(3) PCT.

Claim 15

D2 does not explicitly mention whether the reaction between the carboxyl acid-containing polymeric inhibitor and the polyol takes place under low shear conditions. However, stirring with a magnetic follower which is routinely done during chemical reactions would fall within this concept. Also zero shear can be regarded as within this concept.
Claim 15 does not disclose a comminution step for the solid particles of the scale inhibitor.

Claim 15 is therefore novel.

Drying the scale inhibitor to form a solid and comminuting to obtain an average particle size below 1 μm is known from D1 (col. 2, l. 45-53 and col. 3, l. 6-13).
Hence the method of claim 15 appears to be a routine combination of known features for providing an esterifiable scale inhibitor and for particle formation of a given size.

Claim 15 does not fulfill the requirements of Article 33(3) PCT.

Claim 23

D1 concerns scale inhibition in oil field production (col. 1, l. 6-7).
The scale inhibitor is in the form of a non-aqueous suspension of solid particles which can have an average particle size below 1 μm (col. 2, l. 35-44 and col. 3, l. 6-13). The suspension is injected into a formation preferably via a production well bore which is then shut in for a number of hours to allow it to percolate through the formation (col. 10, l. 19-21).
There is controlled release of the scale inhibitor particles which dissolve at a reduced rate in the fluids present in the formation and the production fluids (col. 10, l. 9-11 and 19-39).
In the case where the point of injection is the production well bore at least some of scale inhibitor particles will be released in the near well bore region of the production well since the suspension of scale inhibitor particles will have percolated through the formation in the near well bore region.
D1 does not appear to disclose that the suspension has an aqueous medium and that it percolates from an injection well towards a near well bore region of the production well since the injection point is the bore well.

Claim 23 is therefore novel.

However, nothing unexpected or critical has been demonstrated for these differences of claim 23 over the prior art.
Claim 23 does not fulfill the requirements of Article 33(3) PCT.

Dependent claims 2-8, 16-19, 21, 22, 24-29 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being as follows:

The feature of claims 2 and 3 are seen in D2 (col. 3, l. 48-52).
The feature of claim 4 is seen in D2 (col. 4, l. 6-13).
The feature of claim 6 is seen in D2 (col. 2, l. 24-25).
The features of claims 7 and 8 are seen in D2 (col. 4, l. 16-24).
The features of claim 21 and 22 are seen in D1 (col. 10, l. 1-5).
The feature of claim 24 is seen in D2.
The feature of claim 29 is seen in D1 (col. 10, l. 37-39).
Nothing critical or unexpected has been demonstrated for the features of the remaining dependent claims.

Article 6 PCT

According to claim 1 the scale inhibitor is esterifiable and is cross-linked with a polyol via ester cross links. Since this feature is in claim 1 it is considered to be an essential feature of the alleged invention. This feature is not seen in independent claim 23, hence an essential feature is missing.

Other points

The units feet, mile, ounce, bbls are not SI units (p. 10, 12, 13, 18 and claims 26, 27).
The PCT does not recognize "incorporated by reference" (p. 3, 7, 9).
The description has not been adapted to the present claims.

Case 9647(2)

Claims:

1. Particles of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links wherein the particles have a mean diameter of less than 1 micron.

2. Particles as claimed in Claim 1 wherein the esterifiable scale inhibitor is carboxylic acid-containing, organophosphorus-containing or organosulfur-containing.

3. Particles as claimed in Claim 2 wherein the carboxylic acid-containing scale inhibitor is selected from the group consisting of homopolymers of an alpha, beta-ethylenically unsaturated carboxylic acid or copolymers containing as one of its components, an alpha,beta-ethylenically unsaturated carboxylic acid.

4. Particles as claimed in Claim 2 wherein the organophosphorus-containing esterifiable scale inhibitor is selected from the group consisting of organophosphates, organophosphonates and polyphosphonates.

5. Particles as claimed in Claim 2 wherein the organosulfur-containing esterifiable scale inhibitor is selected from the group consisting of homopolymers of vinylsulfonic acid, homopolymers of styrene sulfonic acid, copolymers of vinyl sulfonic acid and styrene sulfonic acid, copolymers of vinyl sulfonic acid and AMPS, copolymers of styrene sulfonic acid and AMPS and copolymers of vinyl sulfonic acid, styrene sulfonic acid and AMPS.

6. Particles as claimed in any one of Claims 2 to 5 wherein the esterifiable scale inhibitor is polymeric and has a molecular weight in the range 200 to 20,000, preferably 800 to 10,000.

7. Particles as claimed in any one of the preceding claims wherein the esterifiable scale inhibitor is crosslinked with a polyol selected from the group consisting of

ethylene glycol, glycerol and their higher homologs; dihydroxy-terminated polyethylene oxides or polypropylene oxides; polyvinyl alcohols and co-polymers of vinyl alcohol.

8. Particles as claimed in Claim 7 wherein the polyol has a molecular weight in the range 500 to 130,000, more preferably in the range 5,000 to 50,000.

9. A process for preparing a microgel of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links comprising:
heating, in a reactor vessel, a concentrate comprising water, an esterifiable scale inhibitor, a polyol and a strong acid catalyst under conditions of high shear thereby cross-linking said scale inhibitor and forming a microgel having a mean particle diameter of less than 1 micron.

10. A process as claimed in Claim 9 wherein the shear rate in the reactor vessel is at least 1 ms^{-1}, preferably, at least 5 ms^{-1}.

11. A process as claimed in Claims 9 or 10 wherein the particles of the microgel have a mean diameter in the range 100-750 nm, preferably 200-500 nm.

12. A process as claimed in any one of claims 9 to 11 wherein the concentrate additionally comprises a surfactant.

13. A process as claimed in any one of Claims 9 to 12 which further comprises coating the particles of the microgel with a polymer or wax which dissipates in water or oil above a threshold temperature.

14. A process as claimed in any one of Claims 9 to 13 wherein the microgel is dried to form a dispersible powder comprising microparticles of the esterifiable scale inhibitor crosslinked with the polyol.

15. A process for preparing particles of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links comprising the steps of:

a) heating, in a reactor vessel, a concentrate comprising water, an esterifiable scale inhibitor, a polyol, and a strong acid catalyst under low shear conditions thereby forming a macrogel of the esterifiable scale inhibitor cross-linked with the polyol;

b) drying the macrogel to form a solid; and

c) comminuting the solid to give particles of esterifiable scale inhibitor cross-linked with polyol having a mean particle diameter of less than 1 micron.

16. A process as claimed in Claim 15 wherein the shear rate in the reactor vessel is

less than 0.1 ms^{-1}, preferably less than 0.005 ms^{-1}.

17. A process as claimed in Claims 15 or 16 wherein the dried solid contains less than 0.1 % by weight of water, more preferably less than 0.05 % by weight of water.

18. A process as claimed in any one of Claims 15 to 17 wherein the comminuted particles have a mean diameter in the range 100-750 nm, more preferably 200-500 nm.

19. A process as claimed in any one of Claims 15 to 18 wherein the solid is comminuted in the presence of a polymer which coats the exposed surfaces of the comminuted particles.

20. A suspension comprising particles of an esterifiable scale inhibitor cross-linked with a polyol as defined in any one of Claims 1 to 8 dispersed in a liquid medium.

21. A suspension as claimed in Claim 20 wherein the liquid medium is an oil, an organic solvent or water.

22. A suspension as claims in Claims 20 or 21 wherein the amount of particles dispersed in the liquid medium is the range of from 20 to 50% by weight.

23. A method of inhibiting scale formation in a subterranean formation comprising:
(a) injecting a suspension comprising particles of a controlled release scale inhibitor suspended in an aqueous medium into a formation through an injection well wherein the particles have a mean diameter of less than 1 micron;
(b) allowing the suspension to percolate through the subterrancan formation towards a production well; and
(c) controllably releasing the scale inhibitor from the particles in the near well bore region of the production well.

24. A method as claimed in Claim 23 wherein the particles comprise an esterifiable scale inhibitor crosslinked with a polyol through ester cross-links as defined in any one of Claims 1 to 8.

25. A method as claimed in Claim 24 wherein the particles start to release the scale inhibitor through hydrolysis of the ester cross-links at a temperature of 50 to 150°C.

26. A method as claimed in any one of Claims 23 to 25 wherein the suspension propagates through the formation at a rate of 15 to 100 feet per day.

27. A method as claimed in any one of Claims 23 to 26 wherein the injection well is 0.25 to 1 mile from the production well.

28. A method as claimed in any one of Claims 24 to 27 wherein the esterifiable

scale inhibitor cross-linked with a polyol is continuously dosed into the injection water in an amount in the range 0.01 to 2 weight percent, preferably 0.01 to 0.1 weight percent.

29. A method as claimed in any one of Claims 23 to 28 wherein the amount of scale inhibitor released into the production water is preferably in the range 1 to 200 ppm.